PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23F

A2

(11) International Publication Number: WO 96/27695

(43) International Publication Date: 12 September 1996 (12.09.96)

(21) International Application Number: PCT/EP96/00826

(22) International Filing Date: 29 February 1996 (29.02.96)

(30) Priority Data:
08/397,443 1 March 1995 (01.03.95) US

(71) Applicant (*for all designated States except AT DE*): SANDOZ LTD. [CH/CH]; Lichtstrasse 35, CH-4002 Basle (CH).

(71) Applicant (*for DE only*): SANDOZ-PATENT-GMBH [DE/DE]; Humboldtstrasse 3, D-79539 Lörrach (DE).

(71) Applicant (*for AT only*): SANDOZ-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT MBH [AT/AT]; Brunner Strasse 59, A-1230 Vienna (AT).

(72) Inventors: CURATOLO, Benedict, S.; 6830 Bryden Court, Valley View, OH 44125 (US). MILTENBERGER, Matthew, A.; 4713 Maple Street, Willoughby, OH 44094 (US). VICKERS, Thomas, M., Jr.; 10140 Weathersfiled Drive, Concord Township, OH 44060 (US). WERNET, Judith, H.; 427 Park Place, Berea, OH 44017 (US).

(74) Common Representative: SANDOZ LTD.; Patents & Trademarks Division, Lichtstrasse 35, CH-4002 Basle (CH).

(81) Designated States: CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: A METHOD FOR INHIBITING CORROSION OF REINFORCED CONCRETE

(57) Abstract

A corrosion-inhibiting admixture comprising: i) one or more waterproofing agents; ii) one or more mono-, di- or trialkanolamines; and iii) optionally, one or more additional corrosion-inhibiting agents, with the proviso that if the waterproofing agent is capable of forming a salt with ii) and/or iii), then at least a portion of i) and ii) and/or i) and iii) are present in the admixture in their salt form in combination with each other, which admixture is effective in controlling chloride-induced corrosion of iron or steel reinforcing members in place in concrete without substantially interfering with the ability of the concrete to entrain air.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

A METHOD FOR INHIBITING CORROSION OF REINFORCED CONCRETE

The present invention relates to an admixture formulated to inhibit corrosion in reinforced concrete while providing reproducible and controllable air entrainment response and air stability (ability to maintain the entrainment of air) within the concrete matrix.

Corrosion of reinforced concrete is generally the result of contact with chloride ions which enter the concrete matrix, for example from external application of de-icing chemicals or from marine waters. In order for corrosion to occur there must be three components present, i.e. moisture, chloride ions and oxygen. Inhibiting any one of these components from reacting with the metal reinforcement will substantially decrease corrosion.

US Patent No. 5,262,089 describes a method for inhibiting corrosion in reinforced concrete, comprising adding to a concrete mix an oil-in-water emulsion comprising, as the active corrosion-inhibiting materials, waterproofing materials and an amphoteric compound. Waterproofers are believed to decrease corrosion by waterproofing the concrete matrix, thereby inhibiting moisture and thus chlorides from reaching the metal surface. The amphoteric compound acts as a corrosion inhibitor by passivating the metal surface of the reinforcing bar, i.e. it adsorbs on to and interacts with the metal surface making it less reactive toward corrosion. While this combination is effective in inhibiting corrosion, it generally demonstrates significan, and often deleterious effects on the air-entraining properties of the concrete matrix so that it is difficult to obtain controlled, reproducible air content in concrete containing the oil-in-water emulsion.

EP 0 209 978 describes a method of inhibiting corrosion of iron or steel reinforcing members in concrete which comprises incorporating into a concrete slurry an effective amount of a corrosion-inhibiting admixture which has as its major, and preferably only, ingredient a water-soluble hydroxyalkylamine (alkanolamine). It is stated therein that the hydroxyalkylamines "...do not have a substantial effect upon the air-entraining properties of a cementitious slurry." The alkanolamines are believed to act as corrosion inhibitors by passivating the metal surface, i.e. the alkanolamines adsorb on to and chemically react with the metal surface, making it less reactive toward corrosion. However, alkanolamines by

themselves, while decreasing corrosion, are often not as effective as desired in inhibiting corrosion. Thus, there is a need for an organic corrosion-inhibiting admixture for use in reinforced concrete which will significantly decrease corrosion of the metal reinforcing bars while allowing controlled, reproducible air entrainment within the reinforced concrete matrix.

The present invention provides an organic based admixture comprising a waterproofing agent and an alkanolamine which provides corrosion inhibition along with desirable air entrainment response and stable air content within a reinforced concrete matrix.

Specifically, the present invention provides a method for inhibiting corrosion of iron or steel reinforcing members embedded in concrete, comprising adding to a concrete mix prior to setting an admixture comprising

i) one or more waterproofing agents;

ii) one or more mono-, di- or trialkanolamines; and

iii) optionally, one or more additional corrosion-inhibiting agents, with the proviso that if the waterproofing agent is capable of forming a salt with ii) and/or iii), then at least a portion of i) and ii) and/or i) and iii) are present in the admixture in their salt form in combination with each other, in an amount effective to inhibit corrosion.

In a further embodiment, the present invention provides for a corrosion-inhibiting admixture comprising

i) one or more waterproofing agents;

ii) one or more mono-, di- or trialkanolamines; and

iii) optionally, one or more additional corrosion-inhibiting agents, provided said waterproofing agent is incapable of forming a salt with said mono-, di- or trialkanolamines and/or said additional corrosion-inhibiting agents.

It has been found that iron or steel reinforcing which is used in conjunction with a concrete composition comprising an admixture according to the present invention suffers considerably less from chloride-induced corrosion than does similar reinforcing which is subject to the same environment absent the admixture, or similar reinforcing which is subject to the individual corrosion-inhibiting components of the admixture. In addition, it

has been surprisingly found that the admixtures of the present invention allow for controlled, reproducible air entrainment within the reinforced concrete matrix. The invention therefore also provides a concrete composition adapted to be used in conjunction with metal reinforcing, which composition comprises an admixture of the present invention. There is also provided a method for the protection from corrosion of metal reinforcing in place in concrete comprising the addition to the concrete, prior to pouring and setting in place around the reinforcing, of an admixture of the present invention.

The admixtures of the present invention can be in any physical form, e.g. an emulsion, microemulsion, suspension, solid or solution. The choice of physical form is generally dictated by the specific materials employed in the admixture as well as by the requirements of the particular application in which the admixture will be utilized. Generally, where soluble materials are chosen for the admixture, a solution is employed. For insoluble materials, an emulsion is generally employed, although a microemulsion can be used. The emulsions and microemulsions are prepared by procedures known in the art. If a solid admixture is desired and the chosen materials are not solid, the liquid admixture can be adsorbed on to a solid support using a known inert carrier material such as barium sulphate, silica, silica gel, chalk and clay. Procedures for adsorbing the liquid admixture on to a solid support are well known in the art.

The mono-, di- or trialkanolamines useful in the present invention may be substituted or unsubstituted. Suitable alkanolamines include monoethanolamine, diethanolamine, triethanolamine, aminoethanolamine, diaminoethanolamine, methyldiethanolamine, diethylmethanolamine, dimethylpropanolamine, dimethylaminoethoxyethanol, phenylethanolamine and phenyldiethanolamine. Monoalkanolamines are the preferred alkanolamines, with monoethanolamine being most preferred.

The waterproofing agent can be any material useful as a waterproofer. Preferred waterproofers are those which do not exhibit a deleterious affect on any concrete properties. Examples of suitable materials include hydrocarbons, ester oils, fatty alcohols, fatty amines, fatty acids and salts thereof, fatty amides, silicone compounds, and polymeric materials with a wide variety of chemical compositions. These compounds may be saturated, unsaturated, linear or branched, and aliphatic or aromatic, with a wide range of molecular

weights. The general criterion for the choice of waterproofing material is that it be insoluble in water or form a water-insoluble compound, (e.g. a calcium salt) in the presence of a cement slurry. Ester oils such as butyl oleate and fatty acids such as lauric acid are preferred. Specific examples of waterproofing agents include, but are not limited to, butyl oleate, butyl stearate, glycerol monooleate, 1-dodecanol, oleyl alcohol, decyl alcohol, isostearyl alcohol, 3,7-dimethyl-3-octanol, nonylphenol, 4-dodecylphenol, di-sec-butylphenol, N,N-dimethyl-dodecylamine, trioctylamine, oleylamine, dioctylamine, lauryl dimethyl amine, myristyl dimethyl amine, cetyl dimethyl amine, stearyl dimethyl amine, N-ethyl-3,3-diphenyldipropylamine, 1-dodecyl-2-pyrrolidinone, isostearic acid, linolenic acid, capric acid, myristic acid, oleic acid, salts of the foregoing acids, N,N-dimethyldodecanamide, silicone oil (polydimethylsiloxane), diphenyldimethoxysilane, tetrakis(2-ethylhexoxy)siloxane, decamethylcyclopentasiloxane, diphenylsilanediol, poly(methylphenylsiloxane), octadecyltrimethoxysilane, polybutenes, polybutadienes, PTFE powder, PTFE dispersions, poly(chlorotrifluoroethylene), paraffin, paraffin emulsions, poly(vinyl ethyl ether), tung oil, canola oil, and soy oil.

It should be understood that when the waterproofing material is capable of forming a salt with the selected alkanolamine, e.g. where the waterproofing agent is a fatty acid, the waterproofing agent and alkanolamine may be present in the admixture, at least in part depending upon the quantity of each material employed, as a salt in combination with each other. Similarly, where the waterproofing material is capable of forming a salt with the optional corrosion-inhibiting agent, the waterproofing agent and the optional corrosion-inhibiting agent may be present, at least in part depending upon the quantity of each material employed, as a salt in combination with each other.

The alkanolamine(s) and waterproofing agent(s) are generally present in the admixture in a weight ratio of alkanolamine(s) to waterproofing agent(s) of 1:5 to 5:1, preferably 1:2 to 2:1 and more preferably 1:2 to 1.5:1.

In addition to the alkanolamine and waterproofing agent, the admixtures of the present invention may additionally, and preferably do, include at least one optional corrosion-inhibiting agent to enhance the corrosion-inhibiting ability of the admixture. The optional corrosion-inhibiting agents are believed to act synergistically with the alkanolamine(s) in

passivating the metal surface of the reinforcing member.

The optional corrosion-inhibiting agent can be any corrosion-inhibiting agent, other than an alkanolamine or waterproofing material, which is known to be useful as a corrosion inhibitor, provided the inhibitor does not have a deleterious effect on the physical and chemical properties of concrete. Suitable materials include both organic and inorganic corrosion-inhibiting agents such as amines, amphoteric compounds, benzoates, lignosulfonate, hydrazine hydrate, calgon, molybdates, silicates, tungstates, chromates, phosphates, hypophosphites, fluorides, and nitrites. (For a more complete listing of corrosion inhibitors see, e.g., C.C. Nathan, *Corrosion Inhibitors*, National Association of Corrosion Engineers (1973)). The preferred optional corrosion-inhibiting agents are amines and amphoteric compounds, with the amphoteric compounds being particularly preferred. The amines can be any amines useful as corrosion-inhibiting agents such as methylamine, allylamine, n-decylamine, dibutylamine, triethylamine, imidazole and hexamethylenetetramine. The amphoteric compound is any material which has the capacity of acting as either an acid or a base. Suitable materials include n-coco-beta-aminopropionic acid, tryptophan, aspartic acid, l-tyrosine, glutamic acid and sarcosine.

The optional corrosion-inhibiting agent(s), when desired, is/are generally added into the admixture in an amount of 0.1% - 40%, preferably 0.25% to 25% by weight, based on the total weight of the admixture.

The admixtures may also include other materials, such as surfactants, suspending agents, stabilizers, biocidal agents, etc. as desired.

The amount of admixture to be added to the concrete mix according to the present invention will vary depending upon the particular application. Generally, amounts of 10 to 60 oz. per 100 lbs of cement (0.6 to 3.75 Kg. per 100 Kg. cement) are used for liquid admixtures and 0.1 to 4% actives, by weight based on the weight of cement, in the case where solid admixtures are used to obtain effective corrosion inhibition.

The corrosion-inhibiting admixtures of the present invention are useful in minimizing corrosion of metal reinforcing in reinforced concrete while allowing for controlled,

reproducible air entrainment within the concrete matrix. The admixtures of the present invention can be used with any concrete mix customarily used to prepare reinforced concrete and these are added to the concrete mix at any stage prior to placement of the concrete. Preferably, the admixture is added to the concrete mix during batching.

Concrete mixes employing a corrosion-inhibiting admixture of the present invention may also include other admixtures, such as dispersants, mineral-based additives and air entraining agents, provided the additional admixtures do not interfere with the corrosion-inhibiting ability of the admixture.

The following examples are offered in order to further illustrate the present invention and are not intended to be limiting.

EXAMPLE 1

An admixture according to the present invention is prepared by mixing together 58.5 g of ethanolamine, 2.8 g of "Nopalcol" (trade mark) 6-0 (a surfactant commercially available from Henkel Corporation, Ambler, PA), 228.1 g of water, 1.4 g of n-coco-beta-aminopropionic acid (commercially available under the trade name "Deriphat" 151C from Henkel Corporation) and 0.1 g of "Proxel" (trade mark) GXL (a biocide available from ICI America). The resulting vigorously stirred mixture is slowly added to a combination of 58.5 g of butyl oleate and 0.7 g of oleic acid. The resultant mixture is vigorously stirred and then homogenized, using standard art procedures, to form a milky white emulsion.

EXAMPLE 2

Four admixtures according to the present invention are prepared by mixing together lauric acid or potassium laurate, ethanolamine and deionized water in the quantities indicated below, and stirring until the lauric acid is completely dissolved.

	EXAMPLE 2A	EXAMPLE 2B	EXAMPLE 2C	EXAMPLE 2D
Lauric acid	69.3 g	69.3 g	69.3 g	---
Potassium Laurate (30% w/w solution)	---	---	---	1001 g
Ethanolamine	34.8 g	52.2 g	69.3 g	150.8 g
Deionized water	312.3 g	294.9 g	277.7 g	---

EXAMPLE 3

In order to test the effectiveness of admixtures of the present invention as corrosion inhibitors, a series of electrochemical tests are performed on steel specimens placed in solutions containing the emulsion admixture of Example 1, as described hereinafter. For comparison, the electrochemical tests are also run on specimens placed in reference solutions which did not contain any corrosion inhibitor, on specimens placed in solutions containing the individual corrosion-inhibiting components of the emulsion admixture and on specimens placed in two separate solutions, each containing a different commercially-available corrosion-inhibiting admixture.

The following electrochemical tests are performed for each series of specimens:

Potentiodynamic Linear Polarization (LP): LP is a non-destructive, direct current (DC) electrochemical polarization experiment used to determine the polarization resistance of steel specimens in solution. The test procedure uses an applied potential (voltage) of ± 20mV from the natural corrosion potential at a scan rate of 0.1 mV/sec. The polarization resistance, (Rp), is inversely proportional to corrosion rate and is defined as the slope of the data at zero current when plotted with potential as the ordinate and current as the abscissa. Tafel slope data must be used with the polarization resistance to determine the exact corrosion rate.

Potentiodynamic Tafel Scan: The Tafel Scan is a destructive, direct current (DC) electrochemical polarization experiment. The Tafel Scan is similar to the LP experiment, except that the potential scanned is from the natural corrosion potential to +250 mV for the anodic scan or -250mV for the cathodic scan. Analysis of this data provides information concerning the corrosion rate and the rate of the anodic and cathodic reactions (tafel slopes).

From the above electrochemical data, the parameters needed to calculate the corrosion rate were obtained. The corrosion rate, (C.R.), was calculated as follows:

$$C.R. = \frac{k}{R_p}$$

where,

$$k=\frac{\beta_a\beta_c}{2.303\,(\beta_a+\beta_c)}$$

If β_c is diffusion limited, then

$$k=\frac{\beta_a}{2.303}$$

β_a and β_c are mean tafel slope values from statistically significant samples.

In order to carry out the electrochemical corrosion tests, a standard electrochemical cell similar to model K0047, sold by EG & G Princeton Applied Research, Princeton, New Jersey, is used. Each specimen used in the corrosion tests is a 3/8 inch (0.95 cm) diameter by 1/2 inch (1.27 cm.) long right cylinder of 1018 steel having a surface area of approximately 4.85 square centimeters. Each steel specimen is initially sanded with 400 grit silicon carbide paper and then polished to a 600 grit finish. Immediately after sanding, each specimen is dropped into hexane, removed and wiped dry with a clean paper towel and used immediately. Data analysis and experimental control is performed using PARC M352 software.

The actual tests are carried out as follows:

Each cell is cleaned, prior to beginning a test, using standard laboratory procedure and is then rinsed with deionized water and dried. Test solutions are made from reagent grade chemicals and prepared for each cell separately.

The test solutions are saturated $Ca(OH)_2$ solutions designed to simulate a concrete mix water solution. Where used, the corrosion-inhibiting admixtures are added into the dilute alkaline solution for a total volume of 600 mL. The specimens are then placed into the test solutions and allowed to passivate. After a passivation period of 4 hours, sufficient sodium chloride is added to prepare a 0.6 molal sodium chloride solution. Any salt crystals which adhere to the walls of the cells are rinsed into the cells using a minimum amount of deionized water. The mixtures in each cell are then stirred until

dissolved by placing the individual cells on to a magnetic stirrer for approximately three minutes. None of the specimens are removed from the cells during stirring. Electrochemical tests are performed approximately 24 hours after initial immersion of the specimen into the solution.

The corrosion-inhibiting admixture dosage in these tests is determined by assuming the admixture is dosed at one gallon per cubic yard of concrete containing 600 lbs of cement at a water/cement ratio of 0.4 (4.95L per cu. metre of concrete containing 355.76 Kg of cement at a water/cement ratio of 0.4) (240 lbs ≈ 28.8 gallons of water). The admixture was used to replace one gallon of water, so that the dosage was 1/28.8 = 3.5%.

A statistically significant number of specimens are tested for each corrosion- inhibiting admixture and for the reference. The average test results for each of the electrochemical tests performed and the average corrosion rate (C.R.) for each treatment is given in Table 1, below. In the table, kΩ represents kiloohms, mV/Dec represents millivolts per decade, nA/cm² represents nanoamps per centimeter squared, mpy represents mils per year (mils = milliinches), std error represents the standard error of the mean for the calculated corrosion rate and Diff. limit represents diffusion limited.

TABLE 1

Corrosion Inhibitor	Amount	LP Rp kΩ	Tafel Scan Data βa mV/Dec	βc mV/Dec	Icorr nA/cm²	C.R. mpy [Std error]
Reference	---	0.723	212	Diff. limit	17415	13.61 (9.82%)
Deriphat 151 C	0.08 g	8.392	187	Diff. limit	503	1.068 (15.85%)
Ethanolamine	3.5 g	1.068	186	Diff. limit	7060	7.559 (11.34%)
Deriphat 151 C + Ethanolamine	0.08g + 3.5g	12.44	229	422	3884	2.106 (34.4%)
Example 1	21 mL	435.6	276	243	11.77	0.0125 (5.25%)
DCI*	21 mL	153.3	267	101	59.6	0.0250 (17.68%)
Rheocrete® 222**	21 mL	21.3	190	268	380	0. 373 (15.59%)

* DCI is a nitrite based corrosion-inhibiting admixture, available from W.R. Grace and Co., Cambridge, Massachusetts.

** Rheocrete®222 is an organic based corrosion inhibitor, commercially available from Master Builders, Inc., Cleveland, Ohio.

As can be seen from the data in Table 1, the emulsion admixture of the present invention performs substantially better than the reference and the individual components of the admixture, i.e: "Deriphat" 151 C (n-coco-beta-aminopropionic acid) and ethanolamine, by themselves in inhibiting corrosion, and comparably to the commercially-available corrosion inhibitors.

EXAMPLE 4

In order to test the effectiveness of the admixtures of the present invention as waterproofing agents, the admixtures of Examples 1 and 2 are each added to separate concrete mixes on batching. The concrete mixes are prepared by adding 140 g of the corrosion-inhibiting admixture to most of the mix water in an appropriate mixer. To the resulting mixture is added 66.7 lbs (30.25 Kg) of stone (ASTM C-33, No. 57 gradation), 50.9 lbs (23.1 Kg) of sand (Hugo, meeting the requirements of ASTM C-33), 22.2 lbs (10 Kg) of Medusa Type I cement and an adequate amount of MB-VR, an air entraining agent commercially available from Master Builders, Inc., Cleveland, Ohio, to achieve the target air content. The mixer is started and after 30 seconds, 16 oz. (105 mL)/100 lbs (45.36 Kg) cement of Rheobuild® 1000, a dispersant commercially available from Master Builders, Inc., is introduced into the mix. The balance of the mix water is then added and mixing continued for a total of 4 to 5 minutes. Concrete samples (4" x 4" (10.16 cm x 10.16 cm) cubes) having a cement factor (C.F.) of 600 and water to cement ratio (W/C ratio) of 0.38 are prepared as well as 4" x 4" concrete samples having a C.F. of 517 and a W/C ratio of 0.58. The samples are moist cured for 7 days at 70°F, 100% relative humidity (R.H.), followed by air cure for 7 days at 70°F, 50% R. H. The surface of each sample is then sand blasted to remove surface contaminants and to open the surface. The samples are then immersed in salt water (aqueous solution containing 15% by weight of NaCl) for 1 day, removed from the salt water, blotted dry (surface dry) and weighed to see how much moisture is absorbed. The same samples are then immersed in the salt water for 2 additional days, removed, blotted dry and weighed, and then reimmersed in salt water for 4 more days, again removed, blotted dry and weighed. The percent weight gain of the concrete samples at 1, 3 and 7 days is reported in Table

2. The values reported are the average of two samples. The test is also performed on a reference prepared in the same manner except that the concrete does not contain a corrosion-inhibiting admixture. In Table 2 and subsequent Tables, C.F. stands for cement factor, i.e. the number of pounds of cement per cubic yard of concrete, and W/C Ratio is the water to cement ratio of the concrete mix.

TABLE 2

ADMIXTURE	C.F.	W/C RATIO	% WEIGHT GAIN 1-DAY	3-DAYS	7-DAYS
Reference	600	0.38	1.78	1.97	2.05
Example 1	600	0.38	1.04	1.23	1.30
Example 2A	600	0.38	1.13	1.26	1.32
Example 2C	600	0.38	1.15	1.33	1.37
Reference	517	0.58	2.44	2.59	2.65
Example 1	517	0.58	1.30	1.48	1.57
Example 2A	517	0.58	1.96	2.20	2.31
Example 2C	517	0.58	1.97	2.24	2.34

As can be seen from the data in Table 2, the admixtures of Examples 1 and 2 impart enhanced waterproofing to the concrete samples relative to the reference samples which did not contain an admixture of the present invention.

EXAMPLE 5

Concrete samples each containing an admixture (140 g admixture/22.2 lbs (10 Kg) cement) of Example 1 or 2 and having a C.F. of 600 and a W/C Ratio of 0.38 are prepared and cured in accordance with ASTM C 192. The 7-day compressive strength for each of the cured samples is measured in accord with ASTM C 39 and is reported in Table 3. For comparison, a reference concrete sample is prepared in the same manner but did not contain a corrosion-inhibiting admixture of the present invention.

TABLE 3

ADMIXTURE	COMPRESSIVE STRENGTH 7-Days (PSI/MPa)	% of Reference
Reference	6670/46.0	---
Example 1	6780/46.8	102%
Example 2A	6830/47.1	102%
Example 2B	6790/46.8	102%
Example 2C	6300/43.4	94%

EXAMPLE 6

In order to test the affect the corrosion-inhibiting admixtures of the present invention have on the ability of concrete to entrain air, concrete samples are prepared in accordance with Example 5 having a C.F. of 600 and a W/C ratio of 0.38. The concrete samples differ from each other in the admixture added and the amount of air entraining agent (A.E.A.) used as indicated in Tables 4 and 4A. The amount of admixture dosed is indicated as percent (%) actives by weight of cement (% actives by wt. cement). The percent air in the concrete and the slump are measured at 5 and 15 minutes for the examples in Table 4 according to ASTM C 231 and ASTM C 143, respectively. The percent air in the concrete is measured at 4 and 10 minutes according to ASTM C 231 for the examples in Table 4A. The references do not contain any corrosion-inhibiting admixture. In Tables 4 and 4A, cwt = 100 lbs (45.36 Kg) cement.

TABLE 4

Admixture (Amt, % actives by wt cement)	AEA (Amt, oz per cwt/mL/100 Kg)	Air Content (%) 5 min	15 min	Slump (inches/mm) 5 min	15 min
Reference (---)	---	1.7	2.0	8.0/205	1.75/45
Reference (---)	MB-VR (1/65)	6.8	4.5	8.5/215	3.5/90
Example 1 (0.46)	---	3.0	3.4	7.75/200	1.75/45
Example 1 (0.46)	MB-VR (5/325)	8.0	6.4	3.0/75	1.5/40
Butyl oleate (0.23)	---	1.4	1.6	7.5/190	3.25/85
Butyl oleate (0.23)	MB-VR* (15/975)	2.2	8.2	7.5/190	4.75/120
Butyl oleate (0.23) + Deriphat 151 C (0.008)	---	1.6	2.7	7.5/190	4.0/100
Butyl oleate (0.23) + Deriphat 151 C (0.008)	MB-VR* (15/975)	2.3	2.4	8.0/205	7.0/180
Deriphat 151 C (0.008)	---	4.5	7.4	8.5/215	4.5/115
Deriphat 151 C (0.008)	MB-VR* (15/975)	13.6	27+	7.0/180	7.75/200
Ethanolamine (0.23)	---	2.5	2.6	7.25/185	2.0/50
Ethanolamine (0.23)	MB-VR* (1/65)	7.4	3.4	7.25/185	1.25/30

*MB-VR is a commercial air entraining agent, available from Master Builders, Inc., Cleveland, Ohio.

TABLE 4A

Admixture (Amt, % actives by wt cement)	AEA (Amt, oz per cwt/mL per Kg)	Air Content (%) 4 min	10 min
Reference (---)	MB-VR (0.8/52.0)	6.5	3.5
Example 2A (0.34)	---	3.3	3.2
Example 2A (0.34)	MB-VR (0.2/13.0)	4.9	3.2
Example 2A (0.34)	MB-VR (0.3/19.5)	6.2	4.0
Example 2A (0.34)	MB-VR (0.4/26.0)	6.5	3.6

It should be noted that when butyl oleate and combinations of butyl oleate and Deriphat 151 C are used as the corrosion-inhibiting admixtures, the air entraining agent (MB-VR) is used in amounts of 15 oz/cwt because lesser amounts provided no air entrainment response. The air entraining agent (MB-VR) is also used in an amount of 15 oz/cwt with Deriphat 151 C for comparison purposes.

As indicated from the data in Tables 4 and 4A, when only butyl oleate (and MB-VR) is present in the concrete, it is difficult to entrain air initially and then the concrete sample spirals (increases) uncontrollably in percent air content over time. With just Deriphat 151 C (n-coco-beta-aminopropionic acid) (and no MB-VR), the concrete entrains air initially and increases in air content with time. When MB-VR is present with the Deriphat 151 C, the air content spirals uncontrollably. With ethanolamine and MB-VR, the concrete can be easily and controllably air entrained. Surprisingly, concrete containing the admixtures of Example 1 (butyl oleate, Deriphat 151 C and ethanolamine) and Example 2 (lauric acid and ethanolamine) entrain air initially (in the presence of MB-VR) and maintain the air entrainment over time.

It has been found quite unexpectedly that certain of the fatty acid waterproofers, i.e. C_6-C_{18} saturated, straight-chain fatty acids, do not interfere with the ability of concrete to entrain air, and therefore can be successfully used in combination with one or more other corrosion inhibiting agents to obtain effective corrosion inhibition in reinforced concrete without a deleterious effect on air entraining properties. This is in contrast to the unsaturated fatty acids and branched fatty acids which entrain air in concrete in the absence of an air-entraining agent and produce uncontrollable air contents within the concrete over time. The present invention is therefore also directed to a corrosion-inhibiting admixture comprising

i) one or more C_6-C_{18} saturated, straight-chain fatty acids or salts thereof, and

ii) one or more corrosion-inhibiting agent(s), provided said corrosion-inhibiting agent(s) is/are other than an alkanolamine or waterproofing agent and further provided that if the fatty acid is capable of forming a salt with the corrosion-inhibiting agent, then at least a portion of said C_6-C_{18} fatty acid and said corrosion-inhibiting agent are present in the admixture in their salt form in combination with each other. Where the fatty acid forms a salt in combination with the corrosion-inhibiting agent, the quantity of salt present depends on the quantity of each material employed. The invention is further directed to a method for inhibiting corrosion of iron or steel reinforcing members embedded in concrete, comprising adding to the concrete prior to setting the above corrosion-inhibiting admixture.

Preferably the fatty acid is a saturated, straight chain C_8-C_{16} fatty acid, more preferably a saturated, straight chain C_8-C_{14} fatty acid e.g. lauric acid or salts thereof, such as

potassium laurate and salts of lauric acid with organic bases such as imidazole. Once the fatty acid carbon length exceeds about 16 carbon atoms, the fatty acids and their salts tend to be problematic from a formulation standpoint because of their limited solubility in water, while the fatty acids with less than about six carbon atoms are less effective waterproofers and tend to exhibit poor corrosion performance.

The corrosion-inhibiting agent can be any of the optional corrosion inhibiting agents described hereinbefore. Preferably the corrosion-inhibiting agent forms a salt with the fatty acid. If not, a salt of the fatty acid is preferably employed, however, a preformed salt of the fatty acid may be used even where the fatty acid itself would form a salt with the corrosion-inhibiting agent.

Preferably, the corrosion-inhibiting agent is an amine such as imidazole and n-coco-beta-aminopropionic acid or an oxyanion such as nitrite.

The C_6-C_{18} fatty acid(s) or salt(s) thereof and the corrosion-inhibiting agent(s) are generally present in the admixture in a weight ratio of fatty acid(s) to corrosion-inhibiting agent(s) of 20:1 to 1:20, preferably 2:1 to 1:15, and more preferably 2:1 to 1 to 10. The admixture is generally in the form of a solution, although it can be in any physical form, e.g. an emulsion, microemulsion, suspension or solid.

The amount of fatty acid/corrosion-inhibiting admixture to be added to the concrete mix according to the present invention will vary depending upon the particular application, but generally amounts of 10 to 60 oz. per 100 lbs of cement are employed for liquid admixtures and 0.1 to 4% actives, by weight based on the weight of cement, in the case where solid admixtures are used to obtain effective corrosion inhibition. While it is preferable to add the fatty acid and corrosion-inhibiting agent as a single admixture, the two components may be added separately, and it some instances this is necessary because of the incompatibility of the two components.

The present invention is further illustrated by the following example.

EXAMPLE 7

A corrosion-inhibiting admixture is prepared by combining 76.1 g of a potassium laurate solution (30.4% solids) and 11.6 g of imidazole.

In order to test the effect of the abovementioned admixture on the ability of concrete to entrain air, concrete samples are prepared and tested in a similar manner as are those in Example 6, substituting the present admixture for the admixtures used therein. Potassium laureate is also tested as well as a reference concrete sample, prepared without any corrosion-inhibiting admixture. The results are reported in Table 5.

TABLE 5

Admixture (Amt, % actives by wt cement)	AEA (Amt, oz per cwt/mL per Kg)	Air Content (%) 5 min	15 min
Reference	---	2.9	---
Reference	MB-VR (1/65.0)	6.4	4.2
Potassium laurate (0.23)	MB-VR (0.3/19.5)	4.5	---
Example 7 (0.34)	---	3.7	3.7
Example 7 (0.34)	MB-VR (0.3/19.5)	4.5	---
Example 7 (0.34)	MB-VR (0.75/48.8)	10.1	5.0

As can be seen from the data in Table 5, potassium laurate alone and in combination with imidazole does not adversely affect ability of a concrete sample to entrain air. Surprisingly, the air-entraining characteristics of concrete containing potassium laurate are much like the reference concrete sample, easily entraining air and maintaining air entrainment over time.

EXAMPLE 8

Twelve corrosion-inhibiting admixtures according to the present invention are prepared by combining a fatty acid or its salt and imidazole according to the procedure in Example 7. Table 6 indicates the particular fatty acid used to prepare the admixture used in each cement mix. Concrete is prepared as in Example 4, having a C.F. of 600 and a w/c ratio of 0.38, except that some of the samples do not contain the air-entraining agent, MB-VR. The admixtures are dosed at 0.23% by weight of cement (calculated based on the free acid). Salt soak and compressive strength specimens are cast after 10 minutes total mix time. Two reference samples

are also prepared in the same manner except that they do not contain a corrosion-inhibiting admixture; one reference sample with and one without the air-entraining agent. In addition, a comparative sample is prepared in the same manner except that it contains imidazole, dosed in an amount equivalent to that contained in the admixtures containing the fatty acid waterproofers, in place of the corrosion-inhibiting admixture. The percent (%) air and the slump of the fresh concrete are measured at 4 and 10 minutes according to ASTM C 143 and ASTM C 231, respectively, and the 7-day compressive strength of the cured samples is measured in accord with ASTM C 39; the results are reported in Table 6. Separate concrete specimens are subjected to salt water soaking as in Example 4 and the percent weight gain of those specimens at 1, 3 and 7 days is measured and the results are also reported in Table 6.

TABLE 6

			Slump (inches/mm)		Air content (%)		Salt Soak: Weight Gain			Compressive Strength (psi/MPa)
Fatty Acid in the Admixture	Fatty Acid Carbon Length	MB-VR (oz per cwt/ mL per 100kg cement	4 min.	10 min.	4 min.	10 min.	1-day	3-days	7-days	7-days
Reference	----	----	4.25/110	1.50/40	2.0	2.0	1.56%	1.78%	1.93%	6000/41.4
Reference	----	1/65	7.00/180	3.50/90	8.0	4.7	1.72%	1.97%	2.12%	5540/38.2
Compar. (imidazole)	----	----	6.75/170	2.50/65	3.1	2.4	1.62%	1.90%	2.00%	6080/41.9
Caproic Acid	6 carbon	----	4.25/110	2.25/60	2.8	2.5	1.43%	1.71%	1.84%	6000/41.4
Caproic Acid	6 carbon	1/65	5.50/140	1.50/40	5.8	2.6	----	----	----	----
Caprylic Acid	8 carbon	----	4.75/120	2.75/70	5.0	2.4	1.18%	1.42%	1.52%	5430/37.4
Caprylic Acid	8 carbon	1/65	7.00/180	3.50/90	7.8	4.6	----	----	----	----
Capric Acid	10 carbon	----	6.00/150	2.50/65	4.7	2.9	1.13%	1.34%	1.46%	5440/37.5
Capric Acid	10 carbon	1/65	5.00/130	3.00/80	8.0	4.2	----	----	----	----
Lauric Acid	12 carbon	----	4.50/115	2.75/70	3.0	2.6	1.27%	1.51%	1.64%	5660/39.0
Lauric Acid	12 carbon	1/65	6.00/150	3.25/85	6.9	3.3	----	----	----	----
Myristic Acid	14 carbon	----	6.25/160	3.25/85	2.3	2.2	1.27%	1.55%	1.68%	5470/37.7
Myristic Acid	14 carbon	1/65	5.75/145	3.00/75	4.5	2.4	----	----	----	----
Palmitic Acid	16 carbon	----	5.25/135	2.75/70	2.5	2.4	1.40%	1.67%	1.81%	5530/38.1
Palmitic Acid	16 carbon	1/65	7.75/200	4.50/115	6.1	4.5	----	----	----	----

EXAMPLE 9

Structural features (linear vs. nonlinear and saturated vs. unsaturated) of the fatty acid hydrocarbon chain are investigated for their effect on air entrainment in concrete. Concrete samples having a C.F. of 600 and a W/C ratio of 0.38 and containing a fatty acid or salt thereof as indicated in Table 7 (dosed at 0.23% by weight of cement, calculated based on the free acid) are prepared and tested as for potassium laurate in example 7. A reference concrete sample, prepared without a fatty acid, is also prepared and tested. The results are reported in Table 7. The tests are repeated on concrete samples prepared having a C.F. of 517 and a W/C ratio of 0.58, except that Rheobuild®1000 is not added. The results are also reported in Table 7.

TABLE 7

FATTY ACID	FATTY ACID STRUCTURE	FATTY ACID CHAIN LENGTH	AIR CONTENT (%)	
			4 min.	10 min.
		C.F. = 600 W/C = 0.38		
Reference		----	2.5	2.4
K-Palmitate	Saturated/Linear	16 carbon	2.7	2.3
K-Stearate	Saturated/Linear	18 carbon	2.3	2.3
Isostearic Acid	Saturated/Nonlinear	18 carbon	3.8	3.9
K-Isostearate	Saturated/Nonlinear	18 carbon	5.5	6.0
Oleic Acid	Unsaturated/Nonlinear	18 carbon	4.2	4.8
K-Oleate	Unsaturated/Nonlinear	18 carbon	7.2	7.6
		C.F. = 517 w/c = 0.58		
Reference		----	1.7	1.5
K-Palmitate	Saturated/Linear	16 carbon	2.3	1.9
K-Stearate	Saturated/Linear	18 carbon	2.0	1.8
Isostearic Acid	Saturated/Nonlinear	18 carbon	4.0	4.9
K-Isostearate	Saturated/Nonlinear	18 carbon	7.7	9.8
Oleic Acid	Unsaturated/Nonlinear	18 carbon	5.4	5.8
K-Oleate	Unsaturated/Nonlinear	18 carbon	9.5	14.8

As can be seen from the data in Table 7, the samples containing the branched fatty acid (isostearic acid and potassium isostearate) and the unsaturated fatty acid (oleic acid and potassium oleate) cause air to be entrained within the concrete samples, whereas the samples containing the straight chain, saturated fatty acids (potassium palmitate and potassium stearate) act like the reference since they do not entrain air in concrete.

EXAMPLE 10

The effectiveness of four admixtures of the present invention as waterproofing agents is determined, as are their effect on the slump, air content, initial and final set and 28 day compressive strength of concrete, by introducing each of the admixtures into separate concrete mixes on batching. The concrete mixes are prepared by adding, in an appropriate mixer, the corrosion-inhibiting admixtures as indicated in Table 8 to most of the mix water used to prepare the concrete. To the resulting mixture is added 66.7 lbs (30.3 kg) of stone (ASTM C-33, No. 57 gradation), 54.6 lbs (24.8 kg) of sand and 22.2 lbs (10.1 kg) of Type I cement. The mixer is started and after 30 seconds 67.5 mL of Rheobuild® 1000, a dispersant from Master Builders, Inc. is introduced into the mix. The balance of the mix water necessary to prepare concrete having a W/C ratio of 0.45 is then added and mixing is continued for a total of 4 to 5 minutes.

TABLE 8

Admixture	Components	Amount
1	Admixture of Ex. 1	140 mL
2	*Potassium Laurate + Calcium Nitrite**	92.8 g + 420 mL
3	Admixture of Ex. 1 + Calcium Nitrite**	140 mL + 420 mL
4	Potassium Octanoate + Potassium Nitrite	420 mL***

* The potassium laurate was added in the form of an aqueous solution (29.7% w/w)

** Calcium nitrite was added as an aqueous solution (30% w/w)

*** The admixture was added as an aqueous mixture containing 5.3% by weight of potassium octanoate, 39.2% by weight of potassium nitrite and 2.47% by weight of hexylene glycol defoamer.

The slump (ASTM C 143), air content (ASTM C 231) and initial and final set (ASTM

403) of the fresh concrete mixes are measured and are reported in Table 9. Reference concrete is prepared in the same manner but without a corrosion-inhibiting admixture as well as an additional comparative concrete mix prepared containing 420 mL of a 30% aqueous solution of calcium nitrite in place of the corrosion-inhibiting agent according to the present invention.

TABLE 9

	Slump (in/mm)	Admixture	Initial Set (hrs)	Final Set (hrs)
Reference	3.5/90	2.4	4.8	6.8
Comparative Ex	2.25/55	2.4	3.4	4.5
1	5.0/125	2.7	5.2	6.9
2	2.25/55	2.9	3.4	4.6
3	1.75/45	2.7	3.1	4.2
4	3.25/80	3.6	5.4	7.1

Ten minutes after mixing, 4" X 4" (10.16 cm x 10.16 cm) concrete samples are prepared from each concrete mix. Some of the samples are subjected to an 84-day salt soak study analogous to that carried out in Example 4, and the weight gain at 84 days is indicated in Table 10. Other samples are used to measure the 28-day compressive strength (ASTM C 39), also reported in Table 10. Still further samples are subjected the chloride ion permeability test (performed in accordance with AASHTO T-277). The chloride ion permeability test is a qualitative measure of chloride permeability. The total charge passed in 6 hours is used to rate the concrete's chloride permeability as:

Rating	Total Charge Passed in Coulombs
High	>4000
Moderate	2000-4000
Low	1000-2000
Very Low	100-1000
Negligible	<100

The total charge values are repeatable within ± 100 coulomb for identical concrete mixes.

The results are reported in Table 10. In addition, the preliminary results of a chloride migration experiment are used to calculate a diffusion coefficient for each of the concrete samples containing the corrosion-inhibiting agent according to the present invention as well as the reference and comparative example. The chloride migration experiment is similar to AASHTO T-277, except that a potential of 12V is applied. The smaller potential is applied for several weeks and is used to drive chloride ion through the disk of concrete. The diffusion coefficient is calculated from the flux of chloride through the concrete, however, since steady state flux had not been achieved for all the specimens at the time the diffusion coefficient was calculated, the preliminary diffusion coefficient was determined using the conductivity of the concrete. The diffusion coefficient can be used to calculate the time required to initiate corrosion. The smaller the number, the longer it takes to initiate corrosion. The calculated preliminary diffusion coefficients are reported in Table 10.

TABLE 10

Admixture	28 Day Comp. Strength psi/MPa	84 Day Salt Soak (% wt gain)	Rapid Chloride Permeability (Coulomb)	Preliminary Diffusion Coeff. (cm^2/sec)
Reference	6322/43.6	2.18	2036 (Moderate)	2.23×10^{-8}
Comparative Ex.	7714/53.2	2.20	2883 (Moderate)	2.90×10^{-8}
1	6003/41.4	1.54	2126 (Moderate)	2.05×10^{-8}
2	6742.5/46.5	1.66	2619 (Moderate)	2.73×10^{-8}
3	6597.5/45.5	1.53	2482 (Moderate)	2.69×10^{-8}
4	5205.5/35.9	1.73	2074 (Moderate)	1.67×10^{-8}

The compressive strength data in Table 10 shows that the addition of calcium nitrite increases compressive strength whereas the addition of a waterproofing agent reduces compressive strength, with the presence of both tending to balance each other with respect to compressive strength.

The salt soak data in Table 10 clearly shows that the presence of the waterproofing material

in the admixtures decreases the rate of water absorption and reduces the total water and chloride uptake in the concrete samples. The rapid chloride permeability test and the preliminary diffusion coefficient indicate that the presence of calcium nitrite somehow opens the concrete pore structure to chloride ingress relative to the reference whereas the waterproofing material slows chloride ingress relative to the reference thereby slowing down the corrosion process.

Claims:

1. A method for inhibiting corrosion of iron or steel reinforcing members embedded in concrete, comprising adding to the concrete prior to setting a corrosion-inhibiting admixture comprising
i) one or more waterproofing agents;
ii) one or more mono-, di- or trialkanolamines; and
iii) optionally, one or more additional corrosion-inhibiting agents. with the proviso that if the waterproofing agent is capable of forming a salt with ii) and or iii), then at least a portion of i) and ii) and/or i) and iii) are present in the admixture in their salt form in combination with each other, in an amount effective to inhibit corrosion.

2. A method according to claim 1 wherein said waterproofing agent is an ester oil, preferably butyl oleate, or a fatty acid or salt thereof, preferably lauric acid or a salt thereof.

3. A method according to claim 1 or claim 2 wherein said alkanolamine is a monoalkanolamine, preferably monoethanolamine.

4. A method according to any one of claims 1-3 wherein said corrosion-inhibiting admixture includes said additional corrosion-inhibiting agent(s), preferably selected from the group consisting of an amine and amphoteric compound, the amphoteric compound being preferably n-coco-beta-aminopropionic acid.

5. A method according to any one of claims 1-4 wherein said alkanolamine(s) and said waterproofing agent(s) are present in the corrosion-inhibiting admixture in a weight ratio of alkanolamine(s) to waterproofing agent(s) of 1:5 to 5:1.

6. A corrosion-inhibiting admixture comprising
i) one or more waterproofing agents;
ii) one or more mono-, di- or trialkanolamines; and
iii) optionally, one or more additional corrosion-inhibiting agents, provided said

waterproofing agent is incapable of forming a salt with said mono-, di- or trialkanolamines.

7. A concrete composition adapted to be used in conjunction with metal reinforcing which inhibits the corrosion of the metal, into which concrete composition is incorporated a corrosion-inhibiting admixture comprising

i) one or more waterproofing agents;

ii) one or more mono-, di- or trialkanolamines; and

iii) optionally, one or more additional corrosion-inhibiting agents, with the proviso that if the waterproofing agent is capable of forming a salt with ii) and or iii), then at least a portion of i) and ii) and/or i) and iii) are present in the admixture in their salt form in combination with each other, in an amount effective to inhibit corrosion.

8. A cured concrete structure having one or more iron or steel reinforcing members embedded therein which is formed from a concrete composition to which has been added a corrosion-inhibiting admixture comprising

i) one or more waterproofing agents;

ii) one or more mono-, di- or trialkanolamines; and

iii) optionally, one or more additional corrosion-inhibiting agents, with the proviso that if the waterproofing agent is capable of forming a salt with ii) and/or iii), then at least a portion of i) and ii) and/or i) and iii) are present in the admixture in their salt form in combination with each other, in an amount effective to inhibit corrosion.

9. A method for inhibiting corrosion of iron or steel reinforcing members embedded in concrete, comprising adding to the concrete prior to setting a corrosion-inhibiting admixture in an amount effective to inhibit corrosion, said corrosion-inhibiting admixture comprising

i) one or more saturated, straight-chain C_6-C_{18} fatty acids or salts thereof, and

ii) a corrosion-inhibiting agent , provided said corrosion-inhibiting agent is other than an alkanolamine or waterproofing agent and further provided that if the fatty acid is capable of forming a salt with the corrosion inhibiting agent, then at least a portion of said C_6-C_{18} fatty acid and said corrosion-inhibiting agent are present in the admixture in their salt form in combination with each other.

10. A corrosion-inhibiting admixture comprising

i) one or more saturated, straight-chain C_6-C_{18} fatty acids or salts thereof, and

ii) a corrosion-inhibiting agent , provided said corrosion-inhibiting agent is other than an alkanolamine or waterproofing agent and further provided that if the fatty acid is capable of forming a salt with the corrosion inhibiting agent, then at least a portion of said C_6-C_{18} fatty acid and said corrosion-inhibiting agent are present in the admixture in their salt form in combination with each other.